

Chapter 8

Conclusions

We have studied the dissociation of CO catalyzed by platinum single crystals. At 40 torr of CO, the Pt(111) crystal dissociates CO at 673 K. Under the same conditions, Pt(100) dissociates CO at 500 K, and Pt(557) dissociates CO at 548 K. Hence, the CO dissociation reaction is a structure sensitive reaction. SFG was used to monitor the CO top site resonance as the platinum crystals were heated to the dissociation temperature when exposed to 40 torr of CO. In all three systems, the CO resonance shifts to lower frequency as the platinum crystal is heated. However, the frequency of the CO resonance at the dissociation frequency is lower on the (100) and (111) crystal faces than on the Pt(557) crystal. We believe that the (111) and (100) crystal faces must undergo roughening to expose step or kink sites in order to facilitate the dissociation reaction. This is supported by UHV studies of CO dissociation catalyzed by platinum crystals. These studies observe dissociation only when step or kink sites are present. Since the Pt(111) surface is very stable, it needs to be heated to 673 K to produce the low coordination number sites needed for CO dissociation. Since the Pt(100) surface easily reconstructs, it is able to form the active sites for CO dissociation at relatively low temperatures. The SFG spectra support our conclusion that the CO molecules are sitting on low coordination number platinum atoms at the dissociation temperature. Since the Pt(557) surface already has step sites, the dissociation reaction can take place without

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further roughening of the surface. The CO resonance on the (557) crystal face at the dissociation temperature is at a very similar frequency to CO molecules adsorbed on only the step sites of the crystal. Further studies showed that the dissociation reaction takes place on the (557) surface at CO pressures as low as 1 torr. At 1 torr of CO, the carbon deposition rate is 1.0×10^{-2} ML minute⁻¹. A series of experiments at CO pressures ranging from 5 to 20 torr leads to a 0.8 order dependence of the dissociation reaction on CO pressure.

Further studies were undertaken to investigate the oxidation of CO to CO₂. The production of CO₂ catalyzed by both initially clean and initially carbon covered Pt(557) catalysts was monitored using gas chromatography. Insights into the catalyst's surface composition were deduced through the use of SFG during the high-pressure reactions and by AES post reaction. Below ignition, our results agree with Langmuir-Hinshelwood kinetics. Above ignition, our results indicate that at least two reaction channels exist. The predominant reaction channel is probably mass transport limited, as other studies have indicated. We think that there is evidence of at least one other surface reaction as well, most likely involving the carbon oxide surface species that is evident under certain reaction conditions. We also found that the reaction rate below ignition is higher for the initially carbon covered surface in the presence of equal pressures of CO and O₂ and when exposed to 100 torr of CO and 40 torr of O₂. This indicates that the initially carbon covered catalyst is a very good catalyst for the dissociation of molecular oxygen.

SFG and AES provide evidence for the formation of a carbon oxide surface species under certain reaction conditions. This surface species has been linked to a high

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SFG background, and the reactions that we carried out to characterize the carbon oxide surface species further were discussed in Chapter 6. We also have evidence that this surface species can be reacted away under certain reaction conditions. This may be one of the additional surface reactions that are responsible for the onset of ignition and the high reaction rates above ignition. It was also found that the surface carbon oxide species is a very good catalyst for the dissociation of molecular oxygen and the formation of CO_2 .

In Chapters 4 and 5, we discussed that the dissociation of CO through the Boudouard reaction might be important for the onset of ignition. The experiments carried out in the presence of equal pressures of CO and O_2 provide direct evidence that CO can dissociate in the presence of oxygen. The ignition temperature on the initially carbon covered platinum surface is much lower than on the initially clean platinum surface when exposed to equal pressures of CO and O_2 . This is also evidence that the presence of surface carbon is important in the onset of ignition for the CO oxidation reaction.

While performing the CO oxidation experiments described in Chapter 5, we discovered that the SFG background increased when both carbon and oxygen were present on the Pt(557) surface. The studies described in Chapter 6 were undertaken in order to provide some insight into the nature of this carbon oxide surface and into the nature of the catalytic surface during the oxidation reaction.

Both low pressure and high-pressure experiments were performed. The low-pressure experiments found that, as the SFG background intensity increased, the amount of oxygen relative to carbon on the platinum surface increased. The high-pressure

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experiments showed more complex behavior of the surface species. As the SFG background intensity increased, the amount of oxygen relative to surface platinum decreased. However, the amount of carbon relative to both oxygen and surface platinum first decreased and then increased as the SFG background intensity increased.

TPD studies of the surface prepared during the high-pressure experiments were also performed. These experiments revealed that the low temperature (373 K) surface preparation resulted in a much different catalytic surface from the high temperature preparation (673 K). Comparisons to activated carbon experiments performed by other groups lead us to believe that carboxyl anhydride or a similar molecule might be present on our catalytic surface and responsible for the increase in SFG background. Ultimately, more experiments need to be carried out before any definitive conclusions can be made about the nature of the catalyst surface during the CO oxidation reaction.

In our studies of methane dissociation catalyzed by the Pt(557) single crystal, we found that, in the presence of 40 torr of methane, the platinum catalyst was able to facilitate both methane dissociation and carbon deposition at temperatures as low as 373 K. SFG spectra show that C_xH_y fragments are present on the platinum surface during the high temperature reaction. However, these fragments are too disordered for a definitive assignment. Small amounts of both hydrogen and CO inhibit the deposition of methane on the platinum catalyst. The hydrogen probably rehydrogenates the C_xH_y fragments, inhibiting carbon deposition but not methane dissociation. The CO probably inhibits methane dissociation by blocking the sites needed for the reaction to proceed.

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We also studied fuel rich methane combustion catalyzed by the Pt(557) single crystal. We found that both CO and CO₂ are formed as products during the combustion reaction at temperatures at and above 823 K. Based upon the rate of product formation as a function of temperature and a function of oxygen pressure, we concluded that the CO present in the reaction chamber is probably due to a temperature induced decomposition of CO₂ instead of as a direct result of the methane combustion reaction. Also, although other studies have found the metallic platinum to be the active site for methane combustion, our study found that the experiment took place on a platinum surface covered with multilayers of carbon.